

$S = 1.07$
823 reflections
118 parameters
H-atom parameters not refined
 $w = 1/[\sigma^2(F) + 0.0025F^2]$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O1	0.3970 (5)	0.5842 (4)	0.12462 (17)	0.0663 (19)
O2	0.3624 (5)	0.8306 (4)	0.07665 (18)	0.0682 (19)
O3	1.1612 (5)	0.8732 (3)	-0.12086 (17)	0.0651 (18)
N1	0.9182 (5)	0.7181 (4)	-0.02070 (16)	0.0451 (17)
N2	0.7577 (5)	0.5309 (4)	0.04994 (16)	0.0417 (17)
N3	0.4570 (5)	0.6983 (5)	0.08543 (17)	0.0470 (18)
N4	1.4373 (6)	0.8844 (4)	-0.19648 (19)	0.054 (2)
C1	0.9185 (6)	0.5601 (4)	0.0077 (2)	0.038 (2)
C2	0.6497 (6)	0.6778 (5)	0.04699 (19)	0.041 (2)
C3	0.7445 (6)	0.7955 (5)	0.0046 (2)	0.046 (2)
C4	1.3316 (7)	0.8211 (5)	-0.1409 (2)	0.049 (2)
C5	1.6414 (9)	0.8150 (8)	-0.2148 (3)	0.097 (4)
C6	1.3567 (8)	1.0271 (7)	-0.2393 (3)	0.082 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

O1—N3	1.215 (5)	N3—C2	1.435 (5)
O2—N3	1.221 (5)	N4—C4	1.314 (5)
O3—C4	1.225 (5)	N4—C5	1.458 (6)
N1—C1	1.357 (5)	N4—C6	1.446 (6)
N1—C3	1.357 (5)	C1—C1'	1.446 (7)
N2—C1	1.312 (5)	C2—C3	1.358 (5)
N2—C2	1.358 (5)		
C1—N1—C3	106.8 (3)	N2—C1—C1'	124.8 (3)
C1—N2—C2	103.2 (3)	N2—C2—N3	121.3 (3)
O1—N3—O2	123.7 (3)	N2—C2—C3	112.5 (3)
O1—N3—C2	118.7 (3)	N3—C2—C3	126.2 (3)
O2—N3—C2	117.6 (3)	N1—C3—C2	104.7 (3)
C4—N4—C5	120.7 (4)	O3—C4—N4	125.0 (4)
C4—N4—C6	120.8 (4)	C1—N1—H1	136.4 (8)
C5—N4—C6	118.6 (4)	C3—N1—H1	116.5 (8)
N1—C1—N2	112.8 (3)	C4—O3—H1	125.8 (5)
N1—C1—C1'	122.4 (3)		
D—H...A		D...A	
N1—H1...O3	1.047	1.681	2.699 (4)
			163.2 (11)

The data crystal was sealed in an epoxy-filled capillary tube. The intensity scans were of width $(1.0 + 0.35\tan\theta)^\circ$, with scan speeds of $4\text{--}16^\circ \text{min}^{-1}$. The total exposure time was 14.6 h. The structure was solved by direct methods. The H atoms were constrained to idealized (C—H = 0.95, N—H = 0.90 \AA) positions where the orientation of the methyl groups and the direction of the N—H vector was determined by difference maps. All H atoms were assigned isotropic U values of 0.01\AA^2 plus the value of U of the attached N or C atom.

Data collection: CAD-4-PC (Enraf-Nonius, 1993). Cell refinement: CAD-4-PC. Data reduction: NRCVAX (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: NRCVAX. Program(s) used to refine structure: NRCVAX. Molecular graphics: NRCVAX. Software used to prepare material for publication: NRCVAX.

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Acta Cryst. (1995). **C51**, 2301–2304

(1*S*,8*S*,8*aS*)-(+)-1-(*tert*-Butyldimethylsilyloxy)-8-hydroxy-1,2,3,5,6,7,8,8*a*-octahydro-5-indolizinone

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Abstract

The title compound, $C_{14}H_{27}NO_3Si$, obtained in good yield from a three-step sequence of reactions starting from (4*S*,*SR*)-4-(*tert*-butyldimethylsilyloxy)-3,4-dihydro-5-[(*p*-tolylsulfinyl)methyl]-2*H*-pyrrole, serves as a key intermediate in a study of the total synthesis of (+)-castanospermine. The six-membered lactam ring can be best described as having a distorted envelope conformation.

Comment

In studies leading to the total asymmetric synthesis of the anticancer agent (+)-castanospermine (Hohenschutz, Bell, Jewess, Lewoth, Pryce, Arnold & Clardy, 1981), we synthesized the title compound (1) as a key intermediate utilizing α -sulfinyl ketimine chemistry (Hua, Park, Katsuhira & Bharathi, 1993). Since (1) has not been reported previously and we were unable to prove its relative stereochemistry by NMR spectroscopy, it was necessary to determine its structure unequivocally by single-crystal X-ray analysis before continuing with the synthesis of (+)-castanospermine.

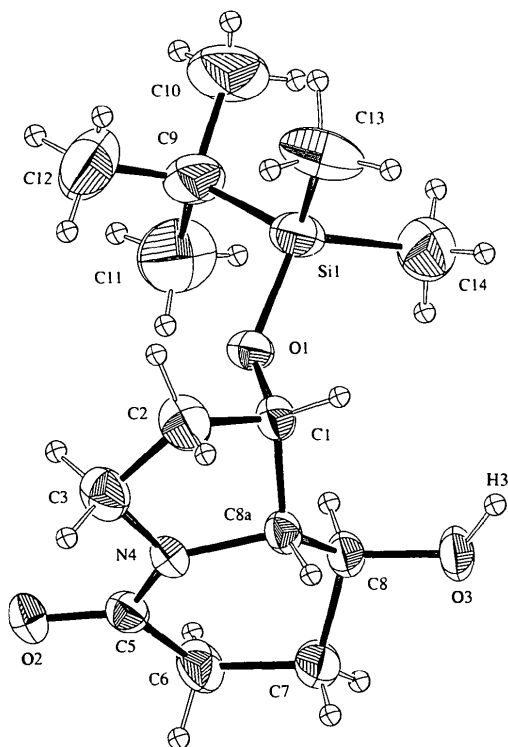
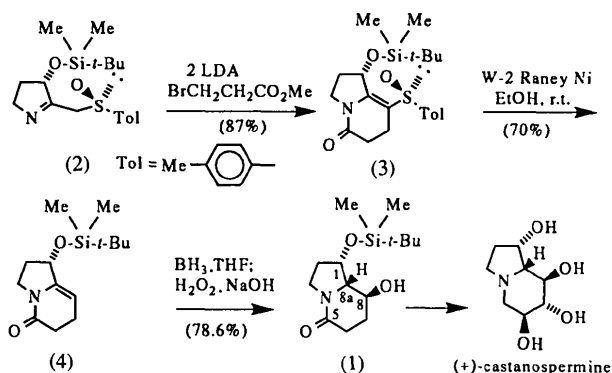


Fig. 1. The molecular configuration and atom-numbering scheme of (1) with displacement ellipsoids at the 30% probability level. H atoms are shown as unlabeled isotropic spheres of arbitrary radii.

Fig. 1 shows the molecular configuration of (1). The N4—C8a bond of 1.486 (7) Å, is slightly longer than the N—C bond of 1.459 (8) Å in a five-membered pyrrolidine ring (Robinson, Hua, Wu, Miao & Meled, 1992). The five-membered ring of (1) possesses a normal envelope conformation. Ring-puckering analysis of the six-membered ring shows that this group should be classified as a distorted envelope conformer (Boeyens, 1978). In the six-membered ring, the five atoms N4, C5, C6, C7 and C8a, are reasonably coplanar, as shown by a least-squares-plane calculation. The C6 atom shows the largest deviation from planarity [0.097 (7) Å]. The C8 atom is 0.688 (7) Å from the least-squares plane composed of atoms N4, C8a, C7, C6 and C5; the angle between the least-squares plane and the plane formed by C7, C8 and C8a is 128.8 (6)°. The lone-pair electrons of N4 and C8a—H are *trans*. The envelope conformation of the lactam ring may be necessary to avoid steric repulsion between the carbonyl O atom and C3—H, and between the bulky C1 silyloxy group and C8—H. Normally, the six-membered lactam ring assumes a distorted chair conformation owing to the tendency of the amide bond to be planar (Barfield & Babaqi, 1987). The molecules are linked *via* O—H...O hydrogen bonds (Table 2) forming infinite chains parallel to [100].

Experimental

All compounds used displayed satisfactory ¹H NMR (400 MHz), ¹³C NMR (100 MHz), UV, IR and low-resolution mass spectra (EI and CI). Compound (1) was synthesized from α -sulfinyl ketimine (2) (Hua, Park, Katsuhira & Bharathi, 1993) in three steps: (i) alkylation followed by ring closure: 2 equiv. of lithium diisopropylamide (LDA) in tetrahydrofuran at 195 K followed by 1 equiv. of methyl 3-bromopropanoate gave sulfoxide (3) (87%); (ii) desulfurization of sulfoxide (3): W-2 Raney nickel in ethanol under 1 atm of hydrogen for 1 h gave olefin (4) (70%); (iii) hydroboration-oxidation of (4): 0.3 ml (0.3 mmol) of BH₃·THF (1M in tetrahydrofuran) was added to a cold (273 K) solution of 54 mg (0.2 mmol) of olefin (4) in 5 ml of tetrahydrofuran under argon. After the solution was stirred at 273 K for 1 h, 0.4 ml of 1N NaOH and 45 μ l of 50% H₂O₂ were added, and the solution was stirred at 298 K for 1 h. The solution was diluted with 50 ml CH₂Cl₂, washed with brine, dried (MgSO₄), concentrated and column chromatographed on silica gel using CH₂Cl₂ and MeOH as eluants to give 44.8 mg (78.6% yield) of (1). Recrystallization of (1) from ethyl acetate-hexane (1:1) gave long white crystals (m.p. 416–417 K) suitable for X-ray analysis; [α]_D²² = +38.1° (*c* = 0.625 in CH₂Cl₂).

Crystal data

C₁₄H₂₇NO₃Si
M_r = 285.46
 Orthorhombic
*P*2₁2₁
a = 7.203 (3) Å
b = 34.626 (5) Å
c = 7.048 (1) Å

Mo *K* α radiation
 λ = 0.71069 Å
 Cell parameters from 24 reflections
 θ = 7.6–12.7°
 μ = 0.132 mm⁻¹
T = 296 K

$V = 1758 (1) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.079 \text{ Mg m}^{-3}$

Prism
 $0.44 \times 0.27 \times 0.19 \text{ mm}$
 Colorless

Data collection

Rigaku AFC-5S diffractometer

$\theta_{\max} = 25^\circ$
 $h = 0 \rightarrow 8$

ω scans (rate: 6° min^{-1} in ω)

$k = 0 \rightarrow 41$
 $l = 0 \rightarrow 8$

Absorption correction: none

3 standard reflections monitored every 100 reflections

1861 measured reflections

reflections

1861 independent reflections

intensity decay: none

1028 observed reflections

$[I > 1.75\sigma(I)]$

Refinement

Refinement on F

$(\Delta/\sigma)_{\max} = 0.0001$

$R = 0.054$

$\Delta\rho_{\max} = 0.24 \text{ e \AA}^{-3}$

$wR = 0.059$

$\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$

$S = 1.80$

Atomic scattering factors

1028 reflections

from *International Tables for X-ray Crystallography*

172 parameters

(1974, Vol. IV, Table

$w = 4F_o^2/\sigma^2(F_o^2)$

2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Si1	0.2002 (3)	0.15677 (6)	0.1921 (3)	0.077 (1)
O1	0.3350 (6)	0.12103 (10)	0.1316 (6)	0.060 (1)
O2	0.8863 (5)	0.06298 (13)	0.1429 (7)	0.071 (2)
O3	0.1725 (5)	0.03184 (13)	0.3553 (7)	0.084 (2)
C1	0.3011 (8)	0.08797 (17)	0.0192 (8)	0.051 (2)
C2	0.4085 (10)	0.0908 (2)	-0.1626 (10)	0.078 (2)
C3	0.6083 (10)	0.0820 (2)	-0.0986 (10)	0.075 (2)
N4	0.5848 (6)	0.05933 (13)	0.0688 (7)	0.046 (2)
C5	0.7255 (9)	0.05268 (2)	0.1859 (10)	0.054 (2)
C6	0.6881 (10)	0.0324 (2)	0.3722 (11)	0.075 (2)
C7	0.4912 (9)	0.0164 (2)	0.3931 (12)	0.074 (2)
C8	0.3529 (8)	0.04654 (18)	0.3214 (10)	0.055 (2)
C8a	0.3854 (7)	0.05274 (19)	0.1117 (9)	0.048 (2)
C9	0.3659 (12)	0.1952 (2)	0.2679 (16)	0.101 (4)
C10	0.2627 (15)	0.2302 (2)	0.3427 (19)	0.16 (1)
C11	0.4891 (15)	0.1801 (3)	0.4287 (17)	0.15 (1)
C12	0.4855 (17)	0.2071 (3)	0.091 (2)	0.19 (1)
C13	0.0502 (14)	0.1703 (3)	-0.0081 (14)	0.129 (4)
C14	0.0481 (13)	0.1430 (2)	0.4005 (14)	0.114 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Si1—O1	1.630 (4)	C3—N4	1.428 (8)
Si1—C9	1.867 (8)	N4—C5	1.327 (7)
Si1—C13	1.838 (9)	N4—C8a	1.486 (7)
Si1—C14	1.894 (9)	C5—C6	1.513 (9)
O1—C1	1.413 (7)	C6—C7	1.530 (9)
O2—C5	1.249 (7)	C7—C8	1.529 (8)
O3—C8	1.416 (7)	C8—C8a	1.511 (9)
C1—C2	1.500 (9)	C9—C10	1.52 (1)
C1—C8a	1.511 (8)	C9—C11	1.53 (1)
C2—C3	1.539 (9)	C9—C12	1.57 (1)
O1—Si1—C9	103.6 (3)	O2—C5—C6	120.5 (6)
O1—Si1—C13	110.1 (3)	N4—C5—C6	118.9 (6)
O1—Si1—C14	110.8 (3)	C5—C6—C7	114.7 (6)
C9—Si1—C13	114.4 (5)	C6—C7—C8	108.9 (5)
C9—Si1—C14	109.2 (4)	O3—C8—C7	107.2 (5)
C13—Si1—C14	108.6 (4)	O3—C8—C8a	111.0 (5)
Si1—O1—C1	131.2 (4)	C7—C8—C8a	108.6 (6)

O1—C1—C2	109.6 (5)	C1—C8a—N4	100.2 (5)
O1—C1—C8a	110.1 (5)	C1—C8a—C8	118.3 (5)
C2—C1—C8a	102.4 (5)	N4—C8a—C8	111.8 (5)
C1—C2—C3	102.6 (5)	Si1—C9—C10	110.9 (7)
C2—C3—N4	103.9 (5)	Si1—C9—C11	109.8 (6)
C3—N4—C5	121.2 (6)	Si1—C9—C12	108.0 (7)
C3—N4—C8a	111.6 (5)	C10—C9—C11	107.5 (9)
C5—N4—C8a	125.8 (5)	C10—C9—C12	109.6 (8)
O2—C5—N4	120.5 (6)	C11—C9—C12	111.1 (8)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...O2 [†]	0.97	1.82	2.767 (6)	165

Symmetry code: (i) $x - 1, y, z$.

Since the configuration at atom C1 of compound (1) is the same as that of the starting material, (4*S*,*SR*)-4-(*tert*-butyldimethylsilyloxy)-3,4-dihydro-5-[(*p*-tolylsulfinyl)methyl]-2*H*-pyrrole (2), whose absolute configuration was previously determined (Hua, Park, Katsuhira & Bharathi, 1993), the absolute total configuration of (1) was established from its stereochemistry as determined by this study. Weak reflections [$I < 10\sigma(I)$] were rescanned (maximum of three rescans) and the counts were accumulated to improve accuracy. The smallest possible horizontal and vertical detector slits were used in order to minimize peak overlap which could result from the long *b* axis. The hydroxyl H3 atom was included in its difference Fourier synthesis position while the remaining H atoms were placed at assumed positions (C—H 0.95 \AA , $U = 1.2U_{eq}$ of the associated atom) and fixed. The rotational orientations of the methyl groups were determined from a difference Fourier synthesis. A degree of disorder is present in the methyl groups as evidenced by their large displacement parameters.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP* (Johnson, 1965) in *TEXSAN*. Software used to prepare material for publication: *TEXSAN FINISH* and *PLATON* (Spek, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram, have been deposited with the IUCr (Reference: FG1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 2304–2305

1,2-Bis(4-pyridyl)ethane

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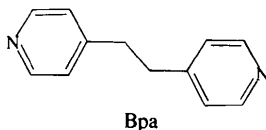
(Received 13 February 1995; accepted 13 April 1995)

Abstract

The 1,2-bis(4-pyridyl)ethane [C₁₂H₁₂N₂ (Bpa)] molecule lies on a centre of symmetry. Bond distances and angles have values within the normal ranges. The value of the torsion angle C2—C3—C6—C6' [−99.5 (3)°] shows that the Bpa molecule is not planar.

Comment

The synthesis of Bpa has been reported by Asword & Burkhardt (1928) and Kutlu (1978). It is of special interest since it is used as a disinfectant in dental hygiene preparations (Edwards, 1973) and dry heat sterilization indicators (Cheng, 1972), and to simulate asphaltene of coal hydroliquefaction (Smith, Romine & El-Sheikh, 1980).



The purpose of the X-ray analysis was to characterize the features of the molecular geometry and conformation. Fig. 1 shows the molecular structure of Bpa and gives the numbering system used. Bond distances and angles lie within the expected ranges and compare well with those found in the structures of [1,2-bis(*N*-ethyl-4-pyridinium)ethane]₂⁴⁺ (7,7,8,8-tetracyanoquinodimethane)₅^{4−} (Ashwell *et al.*, 1977), 1,2-di(4-pyridyl)ethylene-7,7,8,8-tetracyano-*p*-quinodimethane (Ashwell, Kennedy & Nowell, 1983) and TCNQ salts of 1,2-bis(4-pyridinium)ethane (Ashwell, Allen, Cross & Nowell, 1983). The crystal structure viewed along **b** is shown in Fig. 2. The Bpa molecule is on a centre of symmetry.

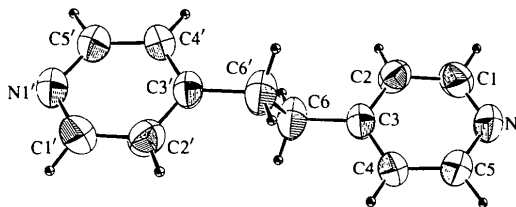


Fig. 1. View of the title molecule. The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level. For clarity, the H atoms are drawn as small spheres of arbitrary size.

The C6—C6' bond distance and C6'—C6—C3 bond angle are 1.498 (4) Å and 112.6 (2)°, respectively. The C2—C3—C6—C6' and C4—C3—C6—C6' torsion angles [−99.5 (3) and 78.0 (3)°, respectively] indicate that the Bpa molecule is not planar.

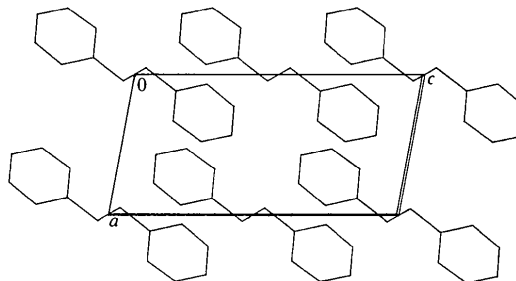


Fig. 2. Projection of the Bpa molecules along **b**.

Experimental

Bpa, from Aldrich Chemical Company, was purified by recrystallization from benzene–cyclohexane (1:3) mixed solvent; m.p. 383 K (literature m.p. 383–384 K).

Crystal data

C₁₂H₁₂N₂
M_r = 184.2

Mo Kα radiation
λ = 0.71073 Å